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# EUROPEAN PATENT APPLICATION

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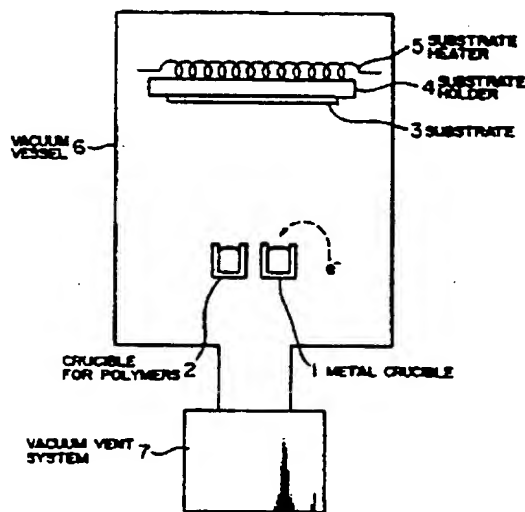
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(54) Amorphous materials.

(57) The present invention provides a novel amorphous material which comprises at least one of a metal and a metalloid and a polymer. Preferably, said metal is selected from the metallic elements of the 2nd, 3rd, 4th, 5th and 6th periods in the periodic table and said metalloid is selected from the group consisting of As, Se, Sb, Si, Ge, Te, Bi and Sn. Said polymer preferably contains 10-1000 carbon atoms. This novel amorphous material can be produced by simultaneous vacuum deposition or sputtering of the metal and/or metalloid and the polymer.

FIG. 1



## AMORPHOUS MATERIALS

### BACKGROUND OF THE INVENTION

The present invention relates to an amorphous material and more particularly, to a novel amorphous material comprising a metal and/or a metalloid and a polymer.

### PRIOR ART

Presence of so-called amorphous metal in which arrangement of atoms is irregular has been well known.

Ordinary metals have crystalline structure where atoms are arranged regularly and systematically, but any metals become amorphous with atomic arrangement disordered when molten at high temperatures. When such metals in amorphous state are cooled in usual manner, they return to the original crystalline state. However, some metals, when quenched, solidify in amorphous state. These metals are amorphous metals.

These amorphous metals are now utilized in various fields. For example, amorphous Si film is used as a solar cell. Besides, amorphous FeSiB soft magnetic film and Co-Zr system amorphous soft magnetic film are being developed as magnetic cores of power transformer and magnetic film materials of magnetic head for magnetic recording, respectively and are practically used in part.

An elemental metal is difficult to become amorphous and hence, amorphous film of metal is obtained by mixing, in molten state, the elemental metal with a metalloid element such as C, B, P, Si, Ge or the like, or with a metal such as Zr, Ta, Hf or the like, and then quenching the mixture. The characteristics of the thus obtained metal amorphous films vary greatly depending on concentration of the added metalloid element or metal such as Zr, Ta, Hf or the like.

These alloys are improved in corrosion resistance and mechanical strength, as compared with those of crystalline metals, but in the case of, for example, Co-Cr magnetic material, addition of materials for amorphization such as above mentioned metalloid elements or Zr, Ta, Hf, etc. cannot provide sufficient amorphous state and/or give enough corrosion resistance.

### SUMMARY OF THE INVENTION

The object of the present invention is to provide a novel amorphous material free from the above mentioned defects of the conventional amorphous films and superior in mass-productivity.

### BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1 and 5 are diagrammatical view of examples of a batch type and continuous type vacuum deposition apparatus used for production of amorphous films of the present invention.

Fig. 2 (a) and (b) are electron diffraction photographs of the amorphous film of the present invention obtained in Example 1 and a simple film of control example.

Fig. 3 is a characteristic graph which shows change in deterioration degree of saturation magnetic flux density with time (day) in which the samples were left in a high temperature and humidity atmosphere.

Fig. 4 is a characteristic graph which shows change in width of scratch given on the surface of samples depending on the number of running of diamond needle.

Fig. 6 is a characteristic graph which shows change of X-ray diffraction peak of Co-Cr at (002) plane when ratio of vapor deposition rate of polyethylene to that of Co-Cr was changed from 0 to 0.19, and Fig. 7 is a characteristic graph which shows change in coercive force in the plane.

## DESCRIPTION OF THE INVENTION

As the results of the inventors' extensive experiments and researches for a long time, it has been found that a novel amorphous material of a structure containing a metal and/or a metalloid and a polymer can be obtained by simultaneous vacuum deposition of a metal or a metalloid and a polymer at a given deposition rate from separate crucibles or hearths. The present invention is based on this finding and knowledge.

Although accurate mechanism has not yet been elucidated, it is considered that in the amorphous material of the present invention, crystallization of metal or metalloid is inhibited to produce amorphous state, since polymer molecules are distributed in metal or metalloid at intervals very close to each other and is present integratedly with metal or metalloid.

In the case of columnar metal particle, it is presumed that some of polymer covers the outer surface of the metal particles, but polymer molecules are relatively uniformly distributed in the metal column at intervals very close to each other. The same thing will be able to be applied to particulate metal. The maximum interval between the polymer molecules, at which the metal and/or metalloid and the polymer cannot become amorphous has not yet been clarified.

Japanese Patent Examined Publication (Kokoku) No. 3137/82 discloses production of a magnetic recording medium having a magnetic recording layer formed by simultaneous deposition of a ferromagnetic substance and a polymer on a support by vapor deposition method.

However, the object of the invention disclosed in the patent publication is to solve the defects of conventional non-binder type ferromagnetic metal films, namely, generation of saw tooth magnetization transfer area and occurrence of noise and reduction of recording magnetization caused by eddy current. According to said invention, since ferromagnetic particles are embedded in polymer and properly dispersed therein, they behave as single magnetic domain particles and magnetic characteristics are improved to solve the conventional defects.

Therefore, the polymer in said invention functions merely as an insulating material and does not provide amorphous materials as in the present invention.

According to the simultaneous vapor deposition method disclosed in the above Japanese patent publication, a magnetic layer is formed which comprises alternately laminated metal layer and polymer layer and it is impossible to produce such state as of the present invention wherein a polymer is relatively uniformly dispersed at intervals very close to each other in a metal.

In any case, an amorphous material comprising a metal and/or a metalloid and a polymer which is contained in the metal or metalloid has not been disclosed in any literatures and is novel.

The term "amorphous material" used here includes not only completely amorphous materials, but also materials containing partially crystalline portion in amorphous substance and materials which are crystallite aggregates which cannot be detected by X-ray diffraction.

It has never been deduced by one skilled in the art before the present invention that a polymer makes amorphous a metal and/or metalloid. Metal or metalloid hardly becomes amorphous by vacuum deposition of simple metal or metalloid alone without using polymer.

Unexpectedly, it has been found that an amorphous film formed by simultaneous vapor deposition of metal and/or metalloid and polymer is markedly superior in corrosion resistance and mechanical endurance to conventional films obtained by deposition of only simple metal and/or metalloid. The accurate reason or mechanism for attainment of improvement in corrosion resistance and mechanical endurance by making metal and/or metalloid amorphous with addition of a polymer has not yet been elucidated.

The amorphous material of the present invention can be formed as a film on a substrate and further can also be used as a mixture prepared by scraping the film from substrate as a powder and mixing it with an appropriate liquid or solid material such as vehicle or binder. According to the latter case, the material can be made into shaped products of various forms at desired time and place by optional means such as coating, spraying or molding.

Therefore, the novel amorphous material of the present invention can be used not only as magnetic materials, solar cells and magnetic cores of power transformers, but also as hydrogen adsorption and desorption metals. The hydrogen adsorption and desorption metals made amorphous by the present invention can be used for construction of power storage system (i.e., a system for storing hydrogen produced by surplus power in hydrogen adsorption and desorption metal and taking out the hydrogen and converting it to electricity when necessary) or high performance power source which utilizes change in hydrogen pressure or high efficiency heat storage system which utilizes emission and adsorption of heat at the time of adsorption and desorption of hydrogen.

The amorphous material of the present invention can be employed for other uses (e.g., amorphous devices, solid image-taking elements) and besides for various uses (e.g., super-conductive materials, etc.)

in which amorphous materials can suitably be used.

As explained above, according to the present invention, various metals or metalloids can be very easily made amorphous by simultaneously vacuum depositing a metal and/or a metalloid and a polymer.

Therefore, the method for producing amorphous material according to the present invention is constitutionally simpler than any conventional methods and apparatus per se used therefor is very simple and practice and operation are also easy.

The amorphous material of the present invention can also be produced by simultaneous sputtering of metal and/or metalloid and polymer.

Metals usable for production of the amorphous material of the present invention include, for example, elements of the 2nd, 3rd, 4th, 5th and 6th Group classified as metallic elements in the Periodic Table. These may be used in the form of simple substance, alloy or compound.

Metalloids usable for the production of amorphous materials of the present invention include, specifically, As, Se, Sb, Si, Ge, Sn, Te and Bi. These may also be used in the form of simple substance, alloy or compound. If necessary, these may be used in admixture with above mentioned metals.

Polymers usable for the production of amorphous materials of the present invention are linear or network polymers having 10-1000, preferably 30-500, more preferably 70-200 carbon atoms. As typical examples thereof, mention may be made of polyethylene, polyethylene terephthalate, polypropylene, polystyrene, polytetrafluoroethylene, polybutadiene, polycarbonate, polyamide, polyimide, polyurethane, polyvinyl chloride, polyvinyl acetate, silicone polymer and the like.

Mixing ratio of metal or metalloid and polymer is generally such that polymer is at least 5 vol%, preferably at least 10 vol%, more preferably 12-40 vol%. When amount of polymer is less than 5 vol%, metal or metalloid cannot be made amorphous. When more than 40 vol%, metal and/or metalloid particles are significantly separated from each other due to the polymer and magnetic characteristics gradually become harder. This is not desired.

The present invention is explained in more detail with reference to the drawings in the following examples.

#### Example 1

An amorphous film was prepared by simultaneous vacuum deposition of Co-Cr and polyethylene using a batch type vacuum deposition apparatus as shown in Fig. 1 under the following conditions. In Fig. 1, 1 and 2 are crucibles for metal and polymer, respectively, 3 is a substrate, 4 is a substrate holder, 5 is a heater for heating the substrate, 6 is a vacuum vessel and 7 is a vacuum vent system.

1. Meta.: Co-Cr
2. Polymer: Polyethylene (average molecular weight: 1000)
3. Substrate: Polyimide film (thickness: 50  $\mu\text{m}$ )
4. Substrate temperature: 150°C
5. Vapor deposition rate: Co-Cr 15 Å/sec
6. Degree of vacuum: 1-2 X 10<sup>-4</sup> Torr

Co-Cr was vapor deposited by electron gun heating and polyethylene was deposited by resistance heating. Thickness of the deposited film was 0.16  $\mu\text{m}$ . Concentration of Cr for Co in the deposited film was 16 wt%.

For comparison, a CoCr simple film was prepared under the same conditions as above except that a degree of vacuum of 1-2 X 10<sup>-5</sup> Torr was employed.

In order to examine whether the thus obtained Co-Cr + polyethylene film of the present invention was amorphous or not, the film was subjected to X-ray diffraction and electron diffraction to find that no peak was seen in the range of  $2\theta = 20^\circ - 100^\circ$  in the X-ray diffraction and only two halo rings appeared in the electron diffraction. Thus, it was recognized that the film was amorphous.

On the other hand, in the case of the Co-Cr simple film, there appeared steep peak at  $2\theta = 44.2^\circ$  due to (002) plane of h.c.p. structure and diffraction pattern was obtained due to h.c.p. structure in electron diffraction. Thus, it was recognized that the film CoCr simple film was crystalline.

Electron diffraction patterns of the Co-Cr + polyethylene film of the present invention and the control Co-Cr simple film are shown in Fig. 2 (a) and (b), respectively. As is clear therefrom, the Co-Cr + polyethylene film of the present invention was amorphous while the control Co-Cr simple film remained crystalline.

Magnetic properties of the Co-Cr + polyethylene film of the present invention and those of the control

Co-Cr simple film were measured. Saturation magnetic flux density  $B_s$  and coercive force  $H_c$  were measured by a vibrating sample magnetometer and anisotropic magnetic field  $H_k$  was measured by a torque meter. The results are shown in the following Table 1.

Table 1

	Saturation magnetic flux density $B_s$ (G)	Coercive force $H_c$ (Oe)	Anisotropic magnetic field $H_k$ (Oe)
Co-Cr-PE film	6200	8.0	54
Co-Cr film	6700	200	5000

In the above Table, the values of coercive force and anisotropic magnetic field are those measured within the face.

As is clear from the results as shown in Table 1, the amorphous Co-Cr + polyethylene film of the present invention had soft magnetic properties.

Moreover, corrosion resistance and mechanical endurance of the Co-Cr + polyethylene film of the present invention and the control Co-Cr simple film were measured.

Corrosion resistance was determined by allowing the films to stand in a high temperature and high humidity atmosphere of 80°C and 90%RH for 10 days and measuring deterioration rate ( $B_s/B_{s0}$ ) of saturation magnetic flux density.  $B_{s0}$  is a saturation magnetic flux density before exposure to the high temperature and high humidity atmosphere and  $B_s$  is a saturation magnetic flux density after exposure to said atmosphere. The saturation magnetic flux density was measured by a vibrating sample magnetometer.

The results are shown in Fig. 3.

As is clear from the graph of Fig. 3, the Co-Cr + polyethylene film of the present invention was hardly corroded even when it was exposed to high temperature and high humidity atmosphere for a long time as compared with the control Co-Cr simple film and thus it will be seen that the film of the present invention is superior in corrosion resistance.

Mechanical endurance was measured in the following manner: The sample film cut to a strip of 10 mm x 50 mm was pasted on a slide glass. A diamond needle (curvature radius of the tip: 50  $\mu$ mR) was allowed to reciprocatingly run on the surface of the sample under a load of 5 gf and at a running speed of 14 m/min and the scratch formed on the surface of the sample was observed by a microscope. Changes in width of the scratch depending on the number of running number are shown in Fig. 4.

As is clear from Fig. 4, width of the scratch on the Co-Cr + polyethylene film of the present invention was narrower than that of the scratch on the control Co-Cr simple film and thus is superior in mechanical endurance.

## Example 2

Amorphous films were prepared by simultaneous vapor deposition of metal and polymer by the continuous type vapor deposition apparatus as shown in Fig. 5 under the following conditions. In Fig. 5, 8 is a crucible for metal, 9 is a crucible for polymer, 10 is a substrate film, 11 is a can roller, 12 is a delivery roller, 13 is a wind-up roll and 14 is a mask.

1. Metal: Fe or Co
2. Polymer: Polyethylene (average molecular weight: 1000)
3. Substrate: Polyimide film (thickness: 50  $\mu$ m)
4. Vapor deposition rate: Fe, Co 500  $\text{\AA}/\text{sec}$

Polymer 150  $\text{\AA}/\text{sec}$

6. Degree of Vacuum:  $2.0 \times 10^{-5}$  Torr

The metal was vapor deposited by electron gun heating and the polymer was vapor deposited by resistance heating. Thickness of the deposited film was 10  $\mu$ m. The polyimide film was a continuous film of

100 m and the amorphous film was deposited along the whole length of the film. Thus, there were obtained two samples of a film of 100 m long having an amorphous film comprising Fe-PE and a film of 100 m long having an amorphous film comprising Co-PE.

In order to examine whether the deposited films of Fe-PE and Co-PE became amorphous or not, 100 test specimens were prepared for each film by cutting each film at an interval of 1 m. All of these test specimens were subjected to X-ray diffraction analysis to find that all of them showed no peaks in the range of angle of diffraction  $2\theta = 20^\circ - 100^\circ$  and they became amorphous.

Magnetic properties were examined on the same specimens in nearly the same manner as in Example 1. The results are shown in the following Table 2.

Table 2

	Saturated magnetic flux density $B_s$ (G)	Coercive force $H_c$ (Oe)	Anisotropic magnetic field $H_k$ (Oe)
Co-PE film	13000	8.0	28
Fe-PE film	15000	2.0	15

In the above Table, the values of coercive force and anisotropic magnetic field are those measured in the plane. The values shown in the Table are average of those obtained on the 100 specimens.

As is clear from the above results, the Co-PE amorphous film and Fe-PE amorphous film of the present invention both showed soft magnetic properties. These properties were very stable along the length of 100 m, namely,  $\pm 5\%$  for  $B_s$ ,  $\pm 20\%$  for  $H_c$  and  $\pm 15\%$  for  $H_k$ .

Upper limit of vapor deposition rate in the Co-PE system is preferably such that which satisfies PE deposition rate/Co deposition rate  $\leq 0.4$ . When it exceeds 0.4, Co particles are remotely separated from each other by PE and magnetic properties become harder, resulting in unfavorable effects.

Thus, according to the method of the present invention which comprises simultaneously vacuum depositing ferromagnetic metal and polymer, there was obtained an amorphous soft magnetic film at high deposition rates which can never be attained by the conventional sputtering method and at a probability of nearly 100%.

As is clear from the above explanation and experimental results, according to the method of the present invention, useful amorphous materials can be mass-produced easily and at low cost.

### Example 3

In this example, changes in degree of amorphousness and magnetic properties of Co-Cr-PE film with change in vapor deposition rate of polyethylene with respect to that of Co-Cr were examined. That is, samples were prepared with changing ratio of deposition rate of polyethylene to that of Co-Cr from 0 to 0.19. Other deposition conditions were nearly the same as those employed in Example 1. (Cr concentration for Co was 24 wt%.)

Changes of peaks at (002) plane according to X-ray diffraction of Co-Cr when ratio of vapor deposition rate of polyethylene to that of Co-Cr was changed from 0 to 0.19 are shown in Fig. 6 and changes of coercive force in the plane are shown in Fig. 7.

From these results, it will be seen that the ratio of vapor deposition rate of polyethylene to that of Co-Cr is desirably at least 0.1 from the point of magnetic properties and at least 0.05 from the point of crystal state according to X-ray diffraction.

As explained hereabove, according to the present invention, a novel amorphous material comprising a metal or metalloid and a polymer is obtained. The novel amorphous material of the present invention can be shaped not only to a film, but also to products of various forms and thus can be employed for a wide variety of uses as compared with conventional amorphous materials composed of only metals.

The amorphous material of the present invention can be produced by a novel method which comprises

simultaneous vacuum deposition of a metal or metalloid and a polymer at a specific ratio of deposition rate. According to the present method, useful amorphous materials can be mass-produced easily, in high yields and at markedly low costs as compared with the conventional various methods for production of amorphous metals.

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## Claims

1. An amorphous material which comprises at least one of a metal and a metalloid, and a polymer.
- 10 2. An amorphous material according to Claim 1 wherein the metal is selected from the metallic elements of the 2nd, 3rd, 4th, 5th and 6th Groups in the Periodic Table and the metalloid is selected from the group consisting of As, Se, Sb, Si, Ge, Te, Bi and Sn.
3. An amorphous material according to Claim 1 wherein the polymer contains 10-1000 carbon atoms.
4. An amorphous material according to Claim 1 wherein amount of the polymer is 5-40 vol%.
- 15 5. An amorphous material according to Claim 3 wherein the polymer contains 30-500 carbon atoms.
6. An amorphous material according to Claim 1 wherein the polymer is at least one member selected from the group consisting of polyethylene, polyethylene terephthalate, polypropylene, polystyrene, polytetrafluoroethylene, polybutadiene, polycarbonate, polyamide, polyimide, polyurethane, polyvinyl chloride, polyvinyl acetate and silicone polymer.
- 20 7. An amorphous material according to Claim 2 wherein the metal is a magnetic metal.
8. An amorphous material according to Claim 7 wherein the metal is at least one of Fe, Co, Fe alloy and Co alloy.
9. A method for producing an amorphous material which comprises simultaneously vacuum depositing or sputtering at least one of a metal and a metalloid and a polymer.
- 25 10. A method according to Claim 9 wherein the metal and the metalloid are in the form of simple substance, alloy or compound.
11. A method according to Claim 9 wherein the metal is selected from the metallic elements of the 2nd, 3rd, 4th, 5th and 6th periods in the periodic table and the metalloid is selected from the group consisting of As, Se, Zb, Si, Ge, Te, Bi and Sn.
- 30 12. A method according to Claim 9 wherein the polymer contains 10-1000 carbon atoms.
13. A method according to Claim 12 wherein the polymer contains 30-500 carbon atoms.
14. A method according to Claim 9 wherein the polymer is at least one member selected from the group consisting of polyethylene, polyethylene terephthalate, polypropylene, polystyrene, polytetrafluoroethylene, polybutadiene, polycarbonate, polyamide, polyimide, polyurethane, polyvinyl chloride, polyvinyl acetate and silicone polymer.
- 35 15. A method according to Claim 9 wherein the metal is a magnetic metal.
16. A method according to Claim 9 wherein the metal is Fe, Co, Fe alloy or Co alloy.

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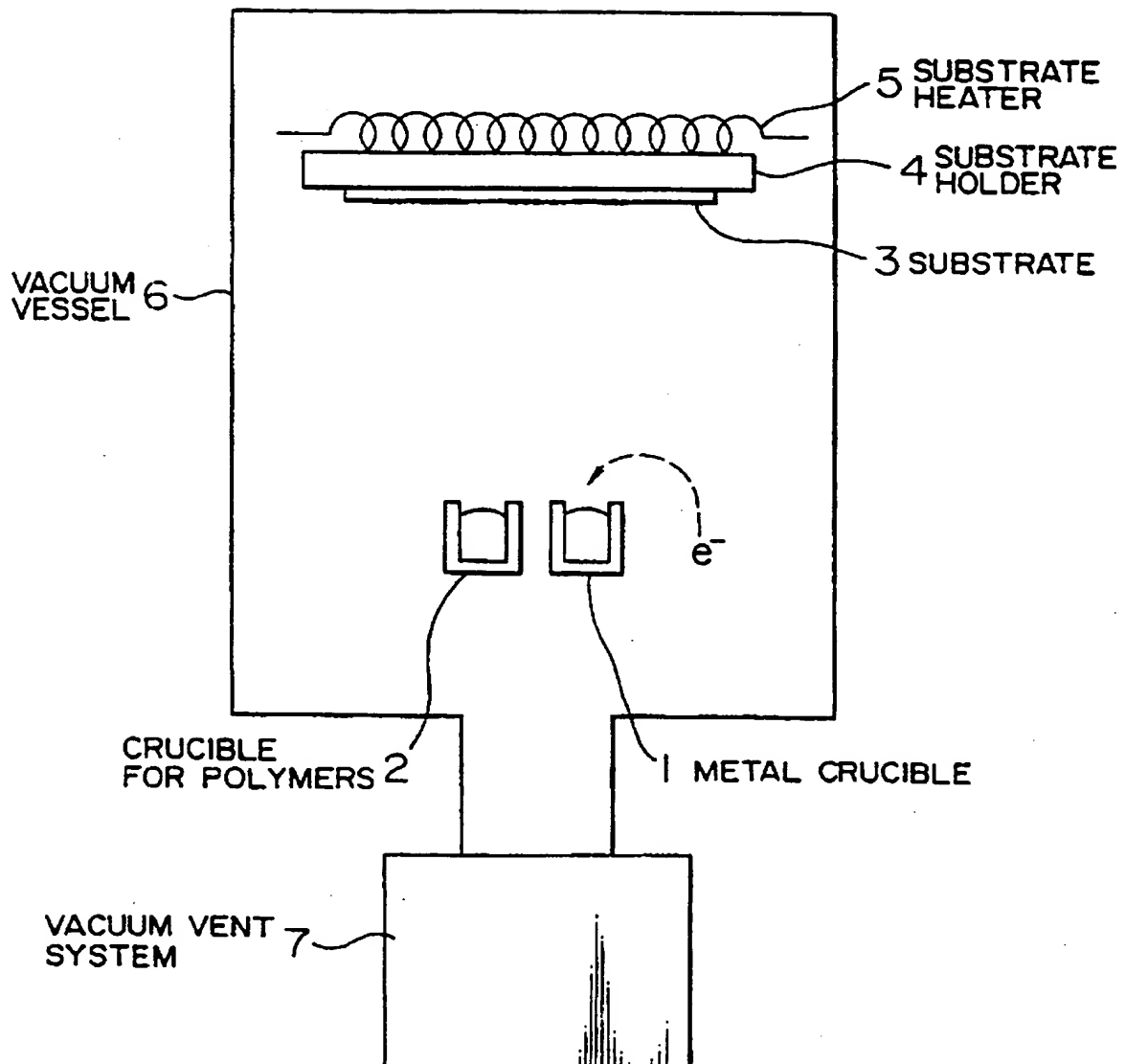
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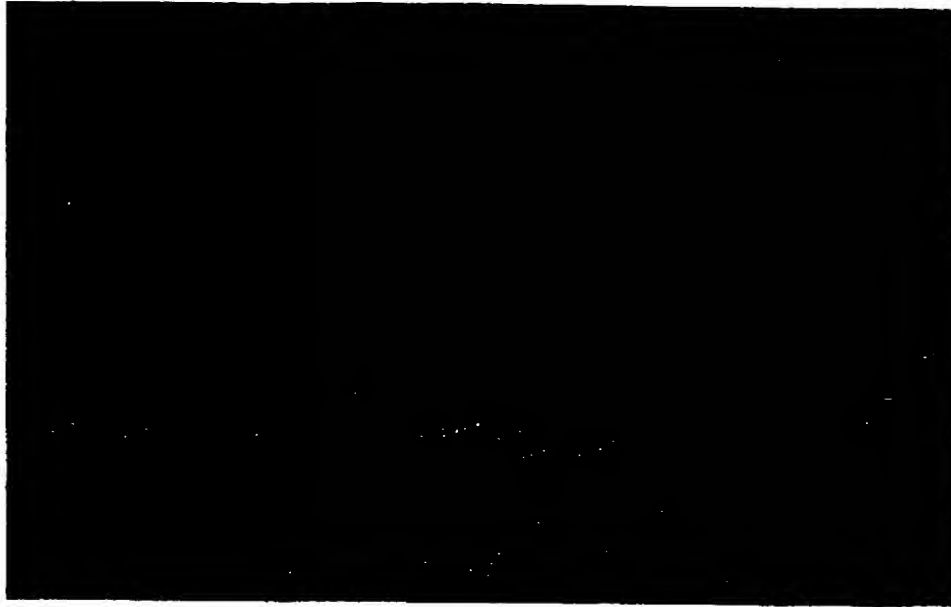
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FIG. 1



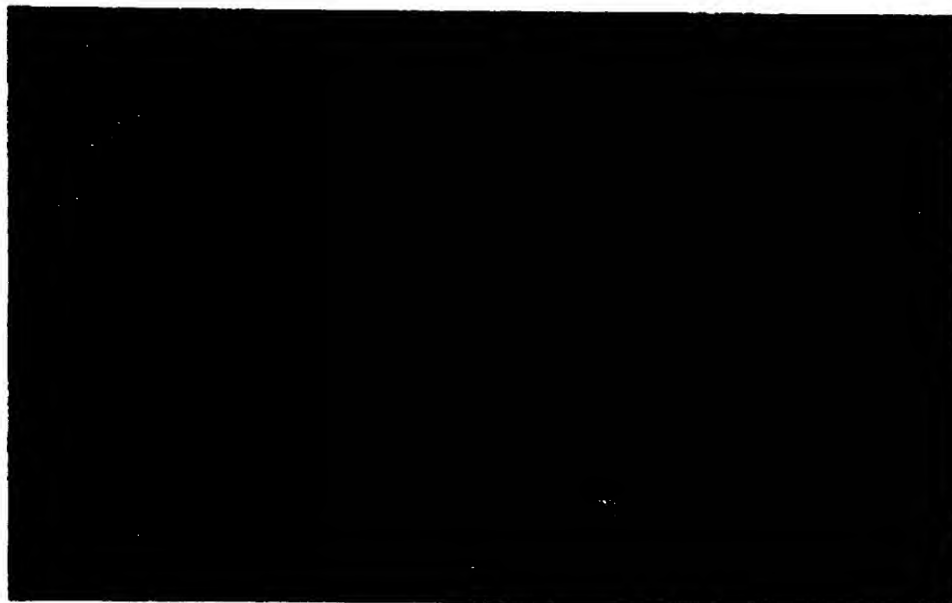
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FIG. 2(a)



ELECTRON DIFFRACTION PATTERN  
OF Co-Cr-PE FILM OF THE PRESENT INVENTION

FIG. 2(b)



ELECTRON DIFFRACTION PATTERN OF Co-Cr SIMPLE  
FILM OF CONTROL EXAMPLE

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FIG. 3

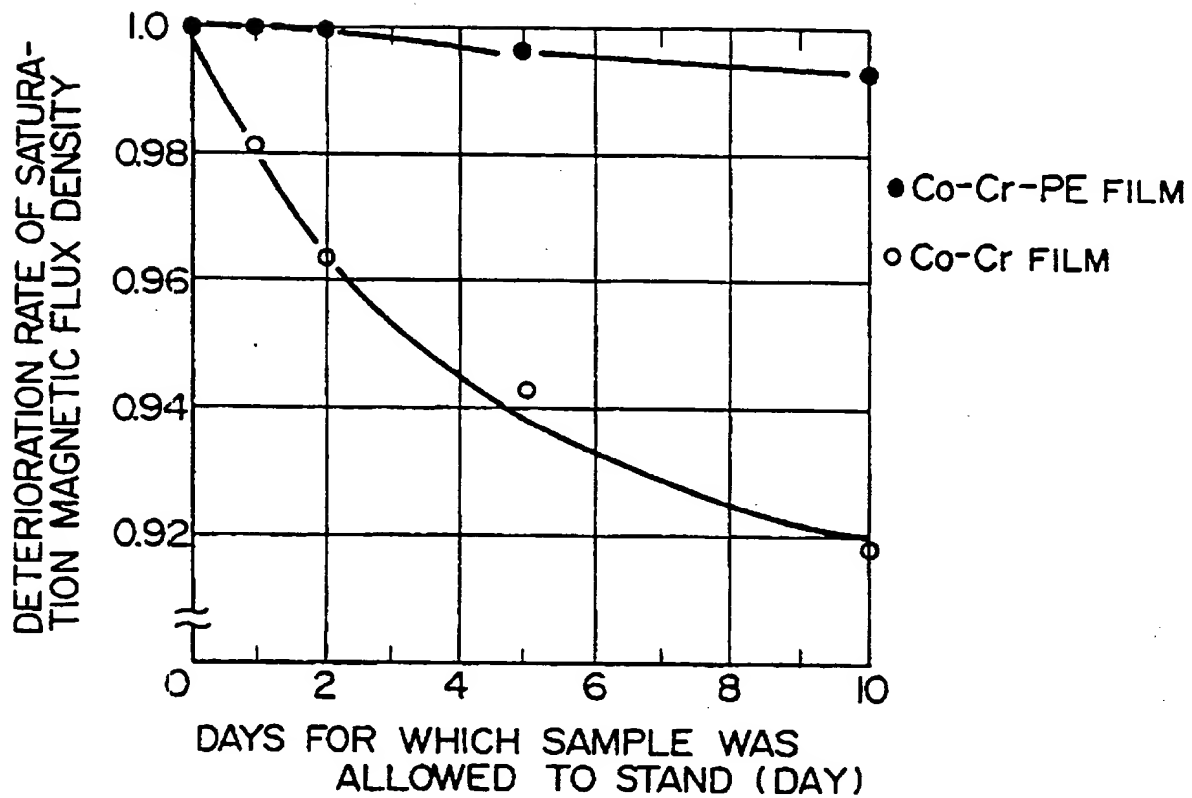
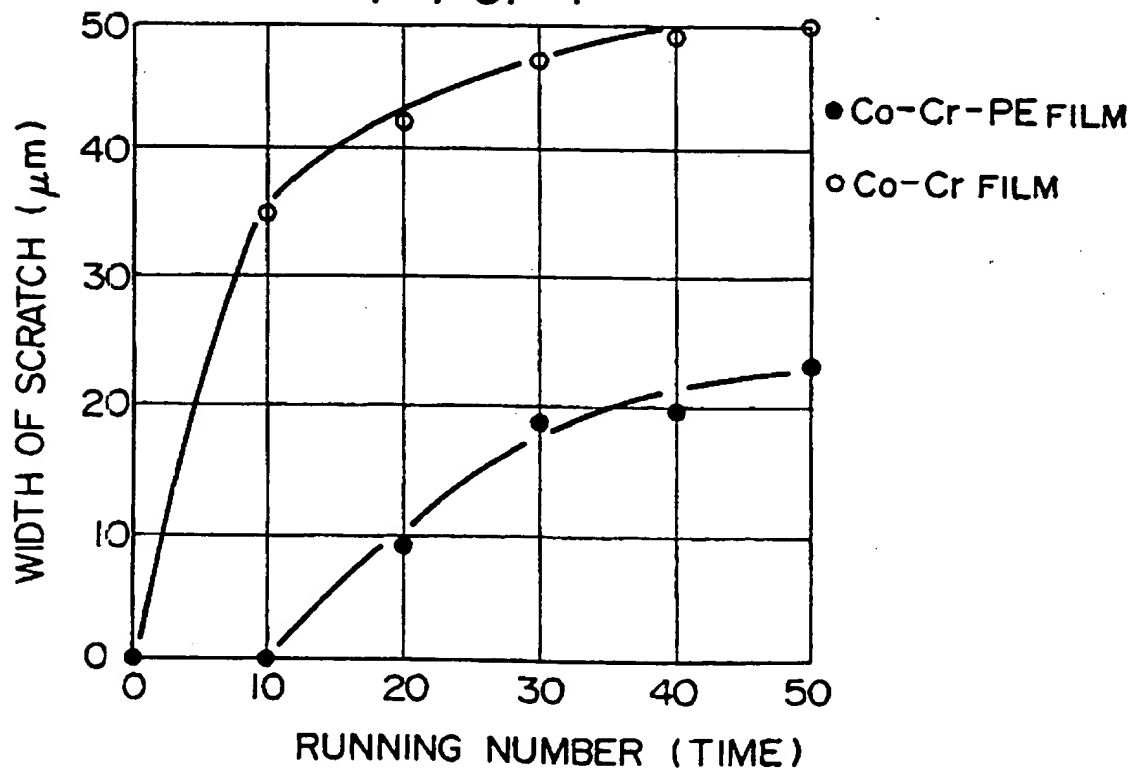
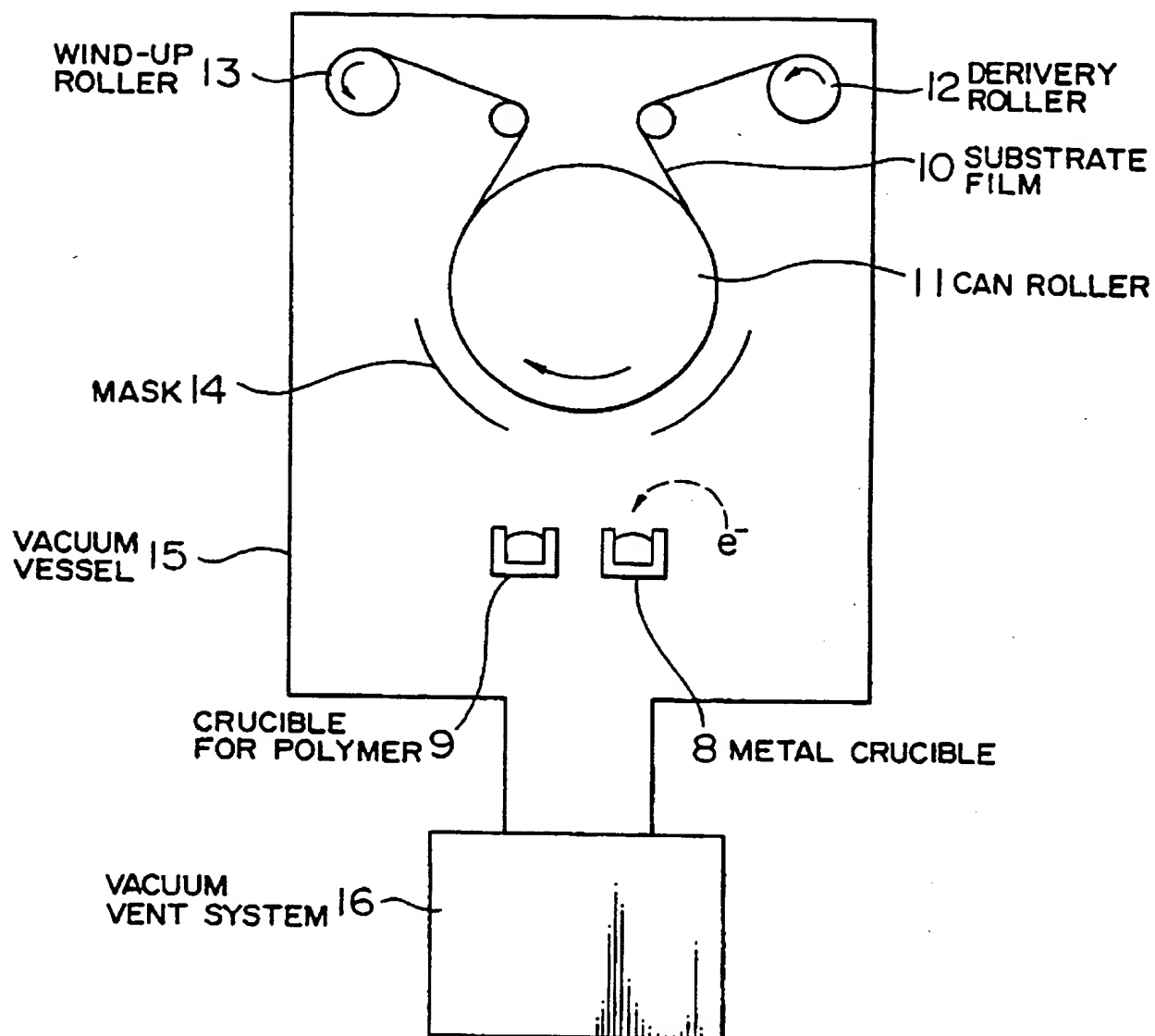


FIG. 4



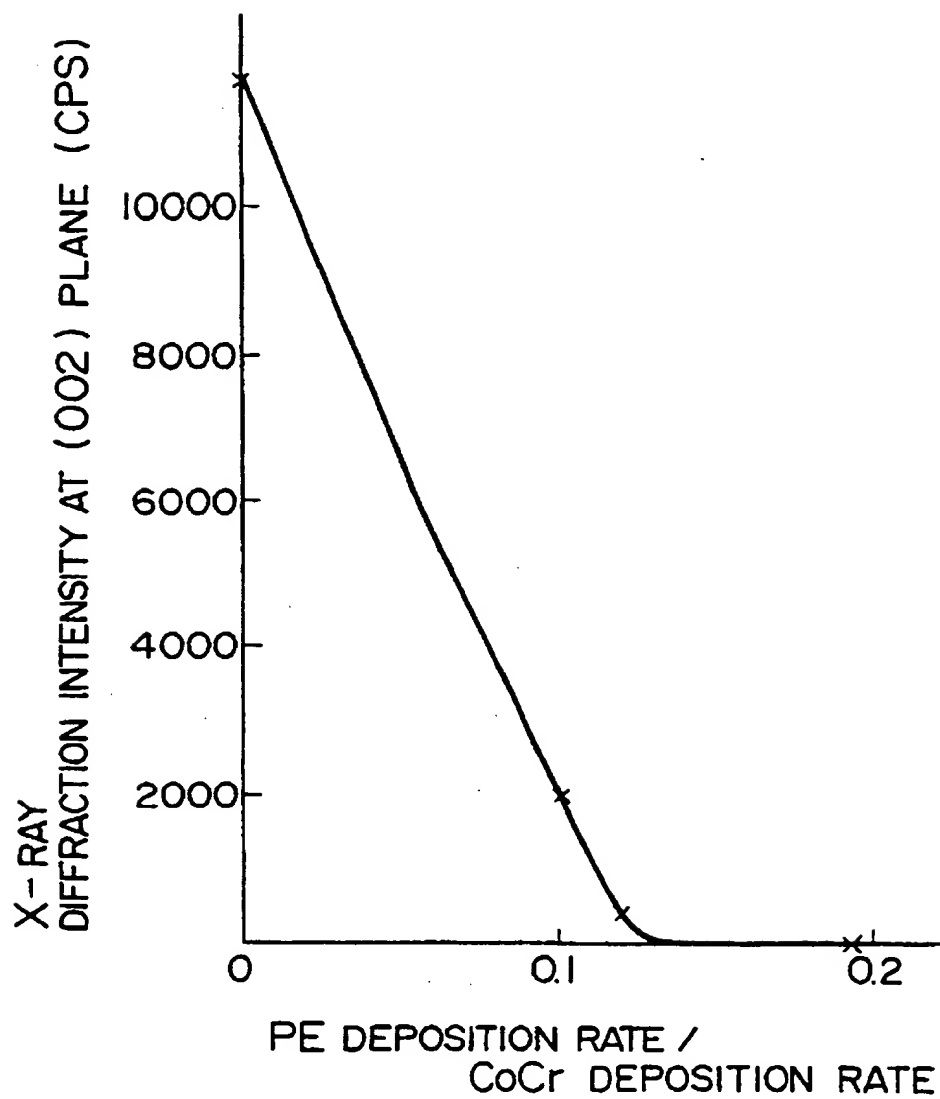
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FIG. 5



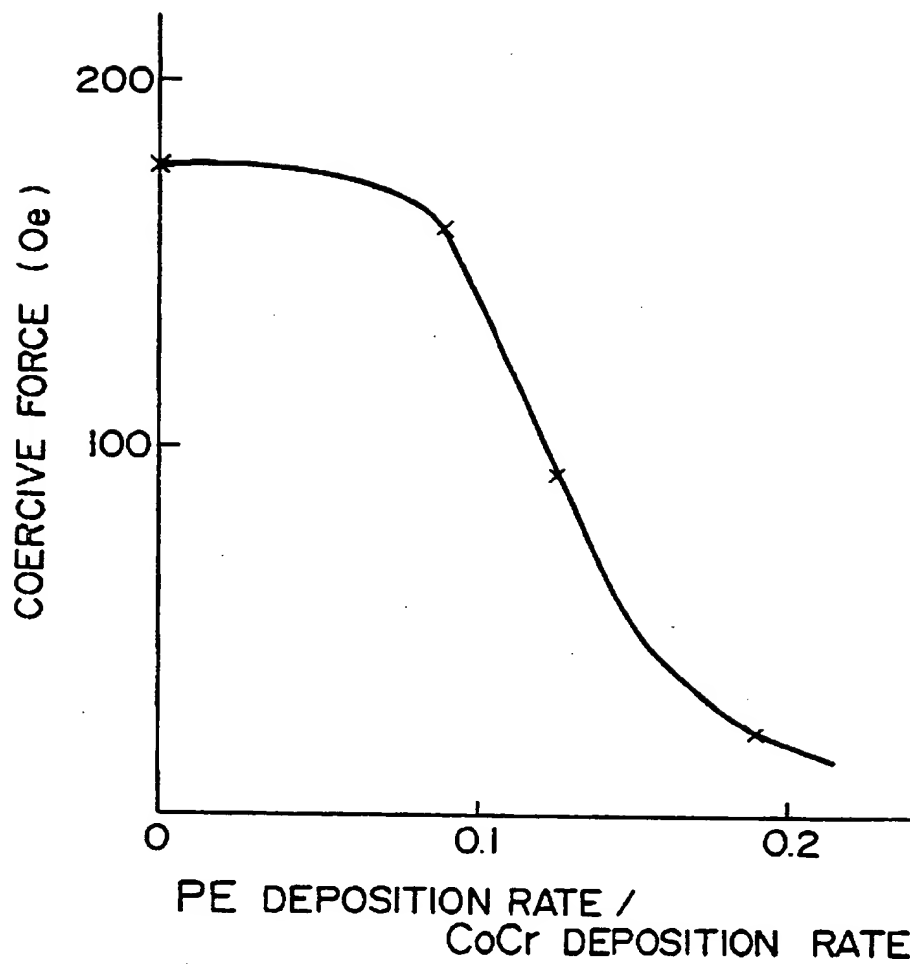
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FIG. 6



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FIG. 7





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## EUROPEAN SEARCH REPORT

Application Number

EP 88 30 0655

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	THIN SOLID FILMS, vol. 105, no. 1, July 1983, pages 1-8, Elsevier Sequoia, Lausanne, CH; Y. ASANO: "Metal-containing plasma-polymerized films" * Page 7, last paragraph * ----	1,2,6	C 23 C 14/06 C 23 C 30/00
A	DE-A-2 511 047 (FUJI PHOTO FILM CO.) * Example 1; claims 1-3 * & JP-B-57 003 137 (08-01-1982) (Cat. D) ----	1-3,5-16	
A	SOLAR ENERGY MATERIALS, vol. 15, no. 1, January 1987, pages 21-35, Elsevier Science Publishers B.V., Amsterdam, NL; L. MARTINU: "Optical response of composite plasma polymer/metal films in the effective medium approach" -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 23 C H 01 F G 11 B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 09-05-1988	Examiner PATTERSON A.M.
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